

# Synthesis of Photo-degradable Polyphthalaldehyde Macromonomer and Adhesive Property Changes of its Copolymer with Butyl Acrylate on UV-irradiation

Hirokazu Hayashi<sup>1\*</sup>, Hideki Tachi<sup>2</sup>, and Kanji Suyama<sup>3\*\*</sup>

<sup>1</sup> Research Division of Applied Material Chemistry,  
Izumi Center, Osaka Research Institute of Industrial Science and Technology (ORIST),

<sup>2</sup> Research Division of Polymer Functional Materials,  
Izumi Center, Osaka Research Institute of Industrial Science and Technology (ORIST),  
7-1 Ayumino-2, Izumi, Osaka 594-1157, Japan,

<sup>3</sup> Faculty of Liberal Arts and Sciences, Osaka Prefecture University,  
1-1 Gakuencho, Nakaku, Sakai, Osaka 599-8531, Japan

\*hayashi@tri-osaka.jp

\*\*suyama@las.osakafu-u.ac.jp

We prepared a new polyphthalaldehyde (PPA) macromonomer by introducing a polymerizable methacryloyl group at the terminal of PPA main-chain. Resulting macromonomer was copolymerized with butyl acrylate to obtain pressure-sensitive adhesives (PSAs). We also compared the behavior of the copolymers with those of polymer blends of poly(butyl acrylate) and linear PPA polymers to clarify the role of polymerization. Higher peel strengths were observed for copolymers than those of corresponding polymer blends. As an increase in irradiation time, the strength generally decreased, although once increased for the copolymer films at the early stage. These results suggest that the introduction and the depolymerization of PPA side-chains caused drastic changes in adhesive properties.

**Keywords:** Polyphthalaldehyde, Photo-degradation, Macromonomer, Peel strength, Pressure-sensitive adhesive

## 1. Introduction

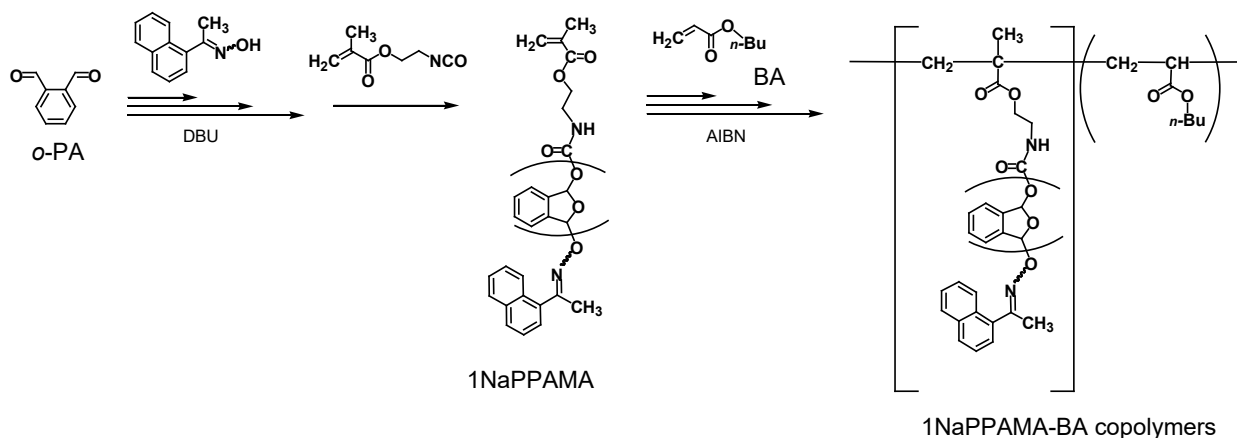
Polyphthalaldehydes (PPAs) are known as self-immolative polymers that can be end-to-end depolymerized (unzipping) [1,2]. Recently, PPAs attract much attention again as a candidate for stimuli-responsive polymers for many applications [3-5].

We have synthesized PPAs with oxime ether terminals, and their photoreactions were investigated [6]. On UV-irradiation both in solution and film state, the depolymerization of the PPAs was confirmed by NMR, UV, and IR spectral measurements. Furthermore, the results of the nanoindentation measurement indicated that the films became elastic on irradiation. Among them, a PPA with 1-acetonaphthone oxime and acetyl terminal (1NaPPA) showed a good depolymerizable

behavior.

In this study, we have prepared a new PPA macromonomer 1NaPPAMA by introducing a polymerizable methacryloyl group at the terminal of PPA main-chain. Also, resulting macromonomer was copolymerized with butyl acrylate (BA) to obtain pressure-sensitive adhesives (PSAs) as shown in Scheme 1.

The performance of PSAs such as tack, peel resistance, and shear resistance generally depends on the viscoelastic properties caused by the balance of storage and loss moduli [7-11]. These properties are provided by soft and hard molecular structures in the PSAs. The latter enables cohesive interaction between polymer chains in the PSA matrixes [12] and have been often introduced in the form of fillers [13-15], side-chains [16-18], and



Scheme 1. Syntheses of 1NaPPAMA and its copolymers with BA.

physically or chemically crosslinking points [19-22].

Because our copolymers 1NaPPAMA-BA involve less flexible and photo-degradable PPA chains, remarkable changes of mechanical property in PSAs are expected. These characteristics are advantageous from the viewpoint of stimuli-sensitive PSAs [23-28]. Although we have already proposed PSAs composed of oxime-ester based photolabile crosslinkers [29], quite different mechanism and behavior are anticipated. We also compared the behavior of the copolymers with those of polymer blends of PBA and linear PPA polymers such as 1NaPPA to clarify the role of polymerization.

## 2. Experimental

### 2.1. General

IR and UV spectra were recorded on Jasco FT-IR4200, and Shimadzu UV1600PC spectrometers, respectively. NMR spectra were measured by JEOL JNM-ECX400 and Bruker BioSpin Ascend 400 spectrometers.

Number ( $M_n$ ) and weight ( $M_w$ ) average molecular weights of polymers were obtained by size exclusion chromatography (SEC) with a Tosoh 8020 liquid chromatography system (Tokyo, Japan) composed of two TSKgel GMH<sub>XL</sub> columns, and a ViscoTech TDA-302 (RI, DP, RALS, LALS) detector with THF eluent and polystyrene standards at 40 °C.

Commercially available reagents were used as received unless otherwise noted. BA, *o*-dichlorobenzene (DCB), tetrahydrofuran (THF), and *N,N*-dimethylformamide (DMF) were subjected to activated alumina columns before use. 1-Acetonaphthone oxime and 1NaPPA were obtained as described previously [6].

### 2.2. Preparation of 1NaPPAMA

In a flask, 4.8 g (35.8 mmol) of *o*-phthalaldehyde (*o*-PA) (SP grade for fluorometry, Nacalai, Kyoto, Japan) and 10 mL of CH<sub>2</sub>Cl<sub>2</sub> (dehydrated grade, Nacalai) was added under argon, and the flask was cooled to -80 °C in an aluminum block cryostat PSL-2500 A (EYELA, Tokyo, Japan). In other vial, 82.4 mg (0.54 mmol) of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 102 mg (0.56 mmol) of 1-acetonaphthone oxime were dissolved in 3 mL of CH<sub>2</sub>Cl<sub>2</sub>. Then, 2.5 mL of the solution was taken out with a syringe and added to the flask dropwise over 20 s, and the mixture was kept stirring at -80 °C for 20 min.

The polymerization was terminated by dropping 1 mL of CH<sub>2</sub>Cl<sub>2</sub> solution containing 72 μL (0.51 mmol) of 2-methacryloyloxyethyl isocyanate (MOI, Showa Denko) over 20 s. After stirring at -80 °C for 10 min, the flask was taken out from the cryostat bath and stirred for 20 min at room temperature. Then, 5 mL of methanol was added to the flask and removed the solvent under reduced pressure to obtain 6.13 g of a white solid. The solid was reprecipitated 5 times from methanol after dissolving in CHCl<sub>3</sub> to afford 3.69 g (Conv. 77 %) of 1NaPPAMA as colorless powder.

### 2.3. Preparation of copolymers of 1NaPPAMA and BA

1NaPPAMA, BA, and 2,2'-azobisisobutyronitrile were dissolved in a solvent and bubbled with N<sub>2</sub> gas. The mixture was heated at 60 °C until the bubbles raised slowly. Obtained copolymers were reprecipitated 5 times from methanol after dissolving in CHCl<sub>3</sub>.

Table 1. Polymerization conditions and characterization of 1NaPPAMA and BA copolymers.

Polymer	In feed (mol %)		In polymer (mol %) <sup>a</sup>			R. T. Conv. (h) <sup>b</sup>	Conv. (%) <sup>c</sup>	$M_n^d$ (kDa)	$M_w^d$ (kDa)
	1NaPPAMA	BA	1NaPPAMA	BA	<i>o</i> -PA : BA				
1NaPPAMA <sub>0.61</sub> -BA	0.15	99.85	0.61	99.39	0.57 : 1	5.5	36	312	559
1NaPPAMA <sub>0.21</sub> -BA	0.050	99.95	0.21	99.79	0.20 : 1	3.7	66	391	1,480
1NaPPAMA <sub>0.05</sub> -BA	0.016	99.98	0.05	99.95	0.05 : 1	6.0	34	266	781
PBA <sup>e</sup>	0	100	0	100	0 : 1	0.8	50	227	787

a) Estimated by <sup>1</sup>H NMR area ratio. b) Reaction time at 60 °C in DCB. c) After reprecipitation. d) From SEC. e) BA homopolymer.

#### 2.4. Peel strength measurement

Polymers were dissolved in toluene (15 wt%), coated on 50 μm PET films with an applicator (200 μm gap), and dried overnight in reduced pressure at room temperature. The thickness of the coated films was estimated to be 30 μm. The films were cut into 10 mm × 80 mm pieces, overlapped with another 2 mm PET plate, and pressed by a roller with 2 kgf. After leaving for 20 min, the films were irradiated with a Hamamatsu Photonics LC5 Hg-Xe lamp (Shizuoka, Japan) through of the PET plate. The light intensity was measured by an Orc UV-M03 illuminometer (Tokyo, Japan) and found to be 150 mW/cm<sup>2</sup> at 365 nm. 180° Peel strength was evaluated using an Instron 5582 Materials Testing System with 100 N loadcell at 300 mm/min. For all samples, 3 runs were carried out.

### 3. Results and discussion

#### 3.1. Synthesis and characteristics of macromonomer 1NaPPAMA

1NaPPAMA was prepared by anionic polymerization of *o*-PA using 1-acetonaphthone oxime as initiator and DBU as a catalyst as described in our previous study [6], except the terminating reagent. In the present study, the polymerization was terminated with MOI which has both isocyanato and methacryloyl groups. Purified polymer was obtained by repeated reprecipitation.

In <sup>1</sup>H NMR spectrum of resulting polymer, small peak at 2.4 ppm assignable to CH<sub>3</sub> unit in oxime moiety is observed along with broad bands (6.4-7.6 ppm) due to aromatic and CH groups in main-chains. Also, small peaks at 1.9, 4.3, 5.6, and 6.1 ppm due to CH<sub>3</sub>, CH<sub>2</sub>, and CH<sub>2</sub>=C groups in MOI moiety appeared. In addition, the UV spectrum of obtained polymer solution has a shoulder around 290 nm due to naphthyl unit. These results clearly show the presence of both

naphthyl and methacryloyl terminals.

From SEC,  $M_n$  and  $M_w$  values were 12.8 and 23.5 kDa, respectively. From  $M_n$  value, the repeating units of *o*-PA in 1NaPPAMA are estimated to be 93.

#### 3.2. Preparation of 1NaPPAMA and BA copolymers

In order to obtain polymers for PSAs, 1NaPPAMA was copolymerized with BA in free-radical mode. In preliminary experiments, we used THF, DMF, and DCB as a solvent. Because DCB afforded the highest yield, we used DCB as a polymerization solvent in further experiments.

The polymerization condition and characteristics of the copolymer with different ratio of 1NaPPAMA and BA are summarized in Table 1. After purification, <sup>1</sup>H NMR spectra showed that both 1NaPPAMA and BA units were successfully incorporated in the copolymers. Based on that 1NaPPAMA contains 93 units of *o*-PA, the ratios of *o*-PA to BA in copolymers are calculated as shown in Table 1. It is estimated that one polymer chain of 1NaPPAMA<sub>0.61</sub>-BA, 1NaPPAMA<sub>0.21</sub>-BA, and 1NaPPAMA<sub>0.05</sub>-BA have 15, 6.4, and 1.0 PPA side-chains, respectively.

#### 3.3. Comparison of copolymers and polymer blends in peel strength

Films of 1NaPPAMA-BA copolymers were prepared for peel strength measurement. Although films of 1NaPPAMA<sub>0.05</sub>-BA were clear, 1NaPPAMA<sub>0.21</sub>-BA and 1NaPPAMA<sub>0.61</sub>-BA gave cloudy and opaque films, respectively.

Peel strengths of 1NaPPAMA-BA copolymers are plotted as a function of irradiation time in Fig. 1. Before irradiation, both 1NaPPAMA<sub>0.21</sub>-BA and 1NaPPAMA<sub>0.05</sub>-BA films showed much higher peel strength compared to PBA, probably due to PPA side-chains which aggregate to form hard segments. In case of 1NaPPAMA<sub>0.61</sub>-BA, the initial peel

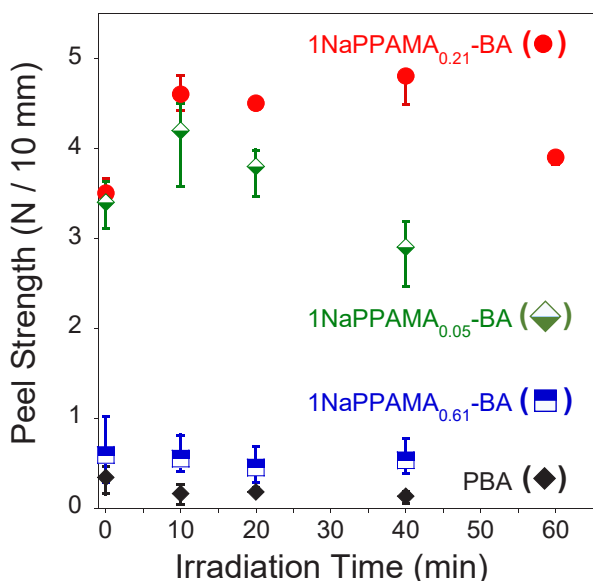


Fig. 1. Peel strength changes of 1NaPPAMA-BA copolymer films on irradiation. Symbols in error bars indicate the averaged values of 3 runs.

strength was 0.6 N as low as PBA, suggesting that too much PPA fraction caused the copolymer harder as a PSA.

On irradiation of 1NaPPAMA<sub>0.21</sub>-BA, peel strengths increased from 3.5 to 4.5 N, and the strength decreased on irradiation for 60 min. Similar trend is observed for 1NaPPAMA<sub>0.05</sub>-BA, where the peel strength once increased on 10 min irradiation and then decreased. Considering that the photo-induced depolymerization of 1NaPPA films proceeded on irradiation for 15 min or above [6], it is expected that photo-degradation of PPA chains in copolymers also proceeds with similar irradiation time. Thus, the increase in peel strength for both copolymers will correspond to the depolymerization of PPA side-chains, although the reason is unknown at present.

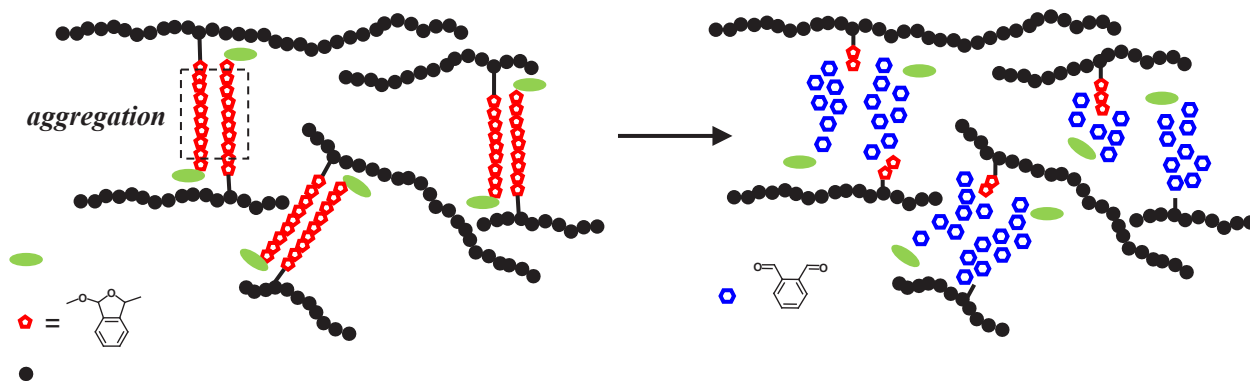


Fig. 2. Schematic illustration of photo-degradation of 1NaPPAMA-BA copolymers.

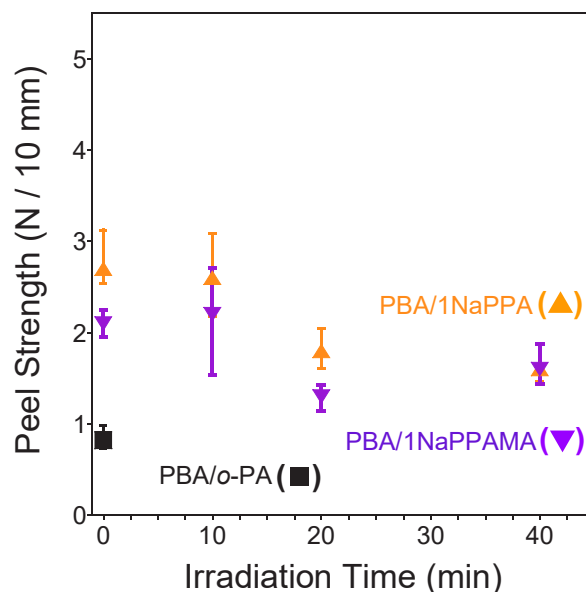


Fig. 3. Peel strength changes of polymer blend films on irradiation. BA unit : *o*-PA unit = 1 : 0.2 (mol/mol). Symbols in error bars indicate the averaged values of 3 runs.

Longer time irradiation caused the decrease in peel strength for both copolymers, which would be due to the disappearance of hard PPA segments as shown in Fig. 2. The degradation of BA main-chains might contribute the decrease, because the slight decrease is often observed for PBA in the previous [29] and present study.

Films of 1NaPPAMA<sub>0.61</sub>-BA did not show the increase in the peel strength. This result suggests that too much PPA side-chains in 1NaPPAMA<sub>0.61</sub>-BA made the matrix glassy to detect the changes of peel strength.

In order to clarify the effect of covalent bonding of PPA chains and BA chains, we investigated the peel strengths of PSAs composed of PBA/1NaPPA and PBA/1NaPPAMA polymer blends with the same ratio of BA to *o*-PA units as

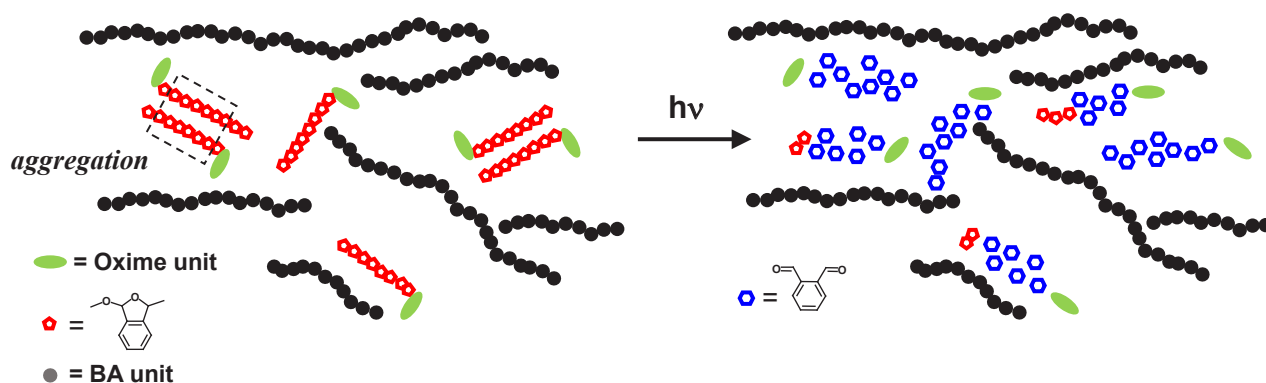


Fig. 4. Schematic illustration of photo-degradation of polymer blends.

that in 1NaPPAMA<sub>0.21</sub>-BA. Figure 3 shows the changes of peel strength of the polymer blends. The initial peel strengths of PBA/*o*-PA, PBA/1NaPPA, and PBA/1NaPPAMA were 0.8, 2.1, and 2.6 N, respectively, located between those of 1NaPPAMA<sub>0.21</sub>-BA and PBA. It was considered that these results were caused by the increase of hard segment in PSA matrixes.

On irradiation, the peel strengths for both PSAs gradually decreased with an increase in irradiation time and got closer to the value of PBA/*o*-PA, 0.8 N. This trend was different from those of 1NaPPAMA<sub>0.21</sub>-BA and 1NaPPAMA<sub>0.05</sub>-BA films as illustrated in Fig. 4.

Failure modes of the PSAs are consistent with this assumption. For copolymers 1NaPPAMA<sub>0.21</sub>-BA, interfacial mode was preferential, although 1NaPPAMA<sub>0.05</sub>-BA and blended polymers detached with cohesive mode. These behaviors did not change before and after irradiation for all coated films.

In conclusion, we have prepared a macromonomer 1NaPPAMA and its copolymers with BA, and investigated the peel strength changes on irradiation to evaluate their pressure-sensitive adhesive properties. Higher peel strengths were observed for copolymers than those of corresponding polymer blends. As an increase in irradiation time, the strength generally decreased, although once increased for 1NaPPAMA<sub>0.21</sub>-BA and 1NaPPAMA<sub>0.05</sub>-BA copolymer films at the early stage. These results suggest that the introduction and the depolymerization of PPA side-chains caused drastic changes in adhesive properties.

#### Acknowledgements

This work was supported by Ogasawara

Foundation. The authors also thank to Dr. Akiko Nakahashi of ORIST for SEC analysis.

#### References

- H. Ito and C. G. Willson, *Polym. Eng. Sci.*, **23** (1983) 1012.
- F. Wang and C. E. Diesendruck, *Macromol. Rapid Commun.*, **39** (2018) 1700519.
- R. E. Yardley, A. R. Kenaree, and E. R. Gillies, *Macromolecules*, **52** (2019) 6342.
- J. P. Lutz, O. Davydovich, M. D. Hannigan, J. S. Moore, P. M. Zimmerman, and A. J. McNeil, *J. Am. Chem. Soc.*, **141** (2019) 14544.
- V. Eriksson, M. A. Trojer, S. Vavra, M. Hulander, and L. Nordstierna, *J. Colloid Interface Sci.*, **579** (2020) 645.
- H. Hayashi, H. Tachi, and K. Suyama, *J. Photopolym. Sci. Technol.*, **33** (2020) 269.
- E. P. Chang, *J. Adhes.*, **34** (1991) 189.
- I. Benedek, "Development and Manufacture of Pressure-Sensitive Products", Marcel Dekker, New York (1998).
- I. Benedek and M. M. Feldstein Ed., "Fundamentals of Pressure Sensitivity", CRC Press, Boca Raton, Florida (2008).
- M. M. Feldstein, E. E. Dormidontova, and A. R. Khokhlov, *Prog. Polym. Sci.*, **42** (2015) 79.
- S. Mapari, S. Mestry, and S. T. Mhaske, *Polym. Bull.*, (2020) DOI: 10.1007/s00289-020-03305-1.
- R. Li, J. A. T. Loontjens, and Z. Shan, *Eur. Polym. J.*, **112** (2019) 423.
- V. G.-Pacios, Y. Iwata, M. Colera, and J. M. M.-Martínez, *Int. J. Adhes. Adhes.*, **31** (2011) 787.
- M. K. Shamsabadi and M. R. Moghbeli, *Int. J. Adhes. Adhes.*, **78** (2017) 155.
- Z. Dastjerdi, E. D. Cranston, and M. A. Dubé,

- Int. J. Adhes. Adhes.*, **81** (2018) 36.
16. S. Yamaguchi, S. Tabuchi, S. Kawahara, and H. Murakami, *Chem. Lett.*, **45** (2016) 463.
  17. S. Yamaguchi, R. Nakanishi, M. Nanchi, S. Kawahara, and H. Murakami, *Chem. Lett.*, **47** (2018) 344.
  18. Y. Wang, F. Weng, J. Li, L. Lai, W. Yu, S. J. Severtson, and W.-J. Wang, *ACS Omega*, **3** (2018) 6945.
  19. C. Fang and Z. Lin, *Int. J. Adhes. Adhes.*, **61** (2015) 1.
  20. C. Fang, Y. Jing, Y. Zong, and Z. Lin, *J. Adhes. Sci. Technol.*, **31** (2017) 858.
  21. Y. Wang, K. Jia, C. Xiang, J. Yang, X. Yao, and Z. Suo, *ACS Appl. Mater. Interfaces*, **11** (2019) 40749.
  22. E. S. Kim, D. B. Song, K. H. Choi, J. H. Lee, D. H. Suh, and W. J. Choi, *J. Polym. Sci.*, **58** (2020) 3358.
  23. R. Vendamme, N. Schüwer, and W. Eevers, *J. Appl. Polym. Sci.*, **131** (2014) 40669.
  24. Q. Chen, Q. Yang, P. Gao, B. Chi, J. Nie, and Y. He, *Ind. Eng. Chem. Res.*, **58** (2019) 2970.
  25. P. Hao, T. Zhao, L. Wang, S. Liu, E. Tang, and X. Xu, *Prog. Org. Coat.*, **137** (2019) 105281.
  26. M. Koike, M. Aizawa, N. Akamatsu, A. Shishido, Y. Matsuzawa, and T. Yamamoto, *Bull. Chem. Soc. Jpn.*, **93** (2020) 1588.
  27. G.-S. Shim, J.-S. Kim, J.-H. Back, S.-W. Jang, J.-W. Park, H.-J. Kim, J.-S. Choi, and J.-S. Yeom, *Int. J. Adhes. Adhes.*, **96** (2020) 102445.
  28. P. Bednarczyk, K. Mozelewska, and Z. Czech, *Int. J. Adhes. Adhes.*, **102** (2020) 102652.
  29. K. Suyama and H. Tachi, *J. Photopolym. Sci. Technol.*, **28** (2015) 45.